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PROSPECTS FOR MARTENSITIC 12%Cr STEELS FOR ADVANCED STEAM POWER PLANTS

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ABSTRACT

Creep strength improvements of martensitic 9%Cr steels have been obtained by controlled additions of V, Nb, N and B to the steels, which resulted in precipitation hardening by fine stable nitrides based on V and Nb as well as in stabilization of Cr carbides against coarsening. The best steels P92 and FB2 are now used in power plants up to 600-620°C steam temperature.

For higher steam temperatures up to 650°C steels with 11-12%Cr are needed for better resistance against steam oxidation. However, fine V and Nb based nitrides may transform to coarse Z-phase (Cr(V,Nb)N) nitrides in steels with such Cr contents, leading to a strength loss in long-term creep.

The paper presents the status of development of new stable 12Cr steels based on the concepts of either strengthening by fine Z-phase nitrides or on elimination of nitrides from the steels.

Keywords: 9-12%Cr steels, Z-phase, creep strength, alloy design

1.0 INTRODUCTION

In the last 30 years materials research focused on the development of improved creep resistant martensitic 9-12%Cr steels for thick section components in advanced highly efficient steam power plants. The introduction of 9%Cr steels P92 and COST FB2 allowed steam parameters to be increased from 250 bar and 540-560°C up to 300 bar and 600-620°C, which is state of the art today.

1.1 Request for improved 12Cr steels

25 years ago there was a strong focus on improving the efficiency of coal fired power plants, and Europe took the lead with the AD700 projects aiming for advanced ultra-supercritical (A-USC) power plants with steam temperatures up to 700°C, based on Ni base alloys in high temperature components.
In the last five years renewable sources like wind and PV have increased dramatically in countries like Denmark and Germany (wind contributed 39% of electricity production in Denmark in 2014). This trend decreases the market opportunities for coal fired power plants, meaning that projects for new plants are very few, and that existing plants have to operate with highly fluctuating output, which increases the fatigue loads on high temperature components. The main potential application for better creep resistant steels in Europe seems to be for replacement components with thinner walls and improved fatigue life.

Globally, there is a strong focus on efficiency improvement of coal fired power plants. Coal is still the dominant source of electricity production, and it is expected to continue to be so in the next decades, since it is the cheapest way to provide electricity to the growing global population [1, 2].

Improvement of steels for steam piping and turbines is the most economical way to increase the efficiency of coal fired power plants. Improved steels would directly enable increased steam parameters of a steel based power plant, since existing steels for other high temperature components in the steam cycle (furnace panels, superheaters) have sufficient properties for higher loads [3].

Improved steels will also be advantageous for A-USC power plants based on Ni base alloys, since increased application temperatures for steels can significantly cut back the necessary amount of expensive Ni-base alloys for such plants.

1.2 Required properties

As a good rule of thumb, a power plant steel or Ni-base alloy should possess 10^5h creep rupture strength of 100 MPa at the maximum application temperature in order to enable sufficiently thin components. At the same time the thermal expansion should be low and the heat conductivity and yield strength should be high in order to protect against thermal fatigue of thick section components. This excludes the use of austenitic steels for this application.
The best available steels, P92 and FB2, have 10^5h creep rupture strengths of 100 MPa at temperatures between 610-630^{0}C, but the higher end of the temperature range is excluded from practical applications due to intensified steam oxidation of the 9%Cr steels.
11-12%Cr is sufficient for protection against steam oxidation up to 650^{0}C, but the requirement for 10^5h creep rupture strengths of 100 MPa at this temperature means that the creep rupture strength should roughly be doubled as compared to P92 and FB2. All attempts to develop 11-12%Cr steel with high creep rupture strength in the last 30 years have resulted in long-term creep rupture strength inferior to P92 due to microstructure instabilities.

It was actually the failure to achieve improved creep rupture strength of 11-12%Cr steels, which led to the idea to use Ni-base alloys and aim for steam temperatures in the 700^{0}C range.

In the present paper a review of basic reasons for the observed microstructure instabilities in 9-12%Cr steels is presented, together with the status of research and ideas for new steel developments to overcome these instabilities.

2.0 MICROSTRUCTURE INSTABILITIES

2.1. Microstructure and strengthening mechanism

The 9-12%Cr steels have tempered martensite microstructures formed during a final normalising and tempering heat treatment, Figure 1, although for some compositions considerable amounts of δ-ferrite may form in the microstructure.

Precipitate hardening should be regarded as the most significant strengthening mechanism to obtain high long-term creep strength in the 9-12%Cr steels [4]. The most frequent precipitates are the Cr carbides $M_{23}C_6$, the intermetallic Laves phases $Fe_2(Mo,W)$ and the MN nitrides (V,Nb)N. Boron addition to the steels may stabilise the $M_{23}C_6$ carbides, especially near the prior austenite grain boundaries [5-7].

2.2 (V,Nb)N nitrides and Cr(V,Nb)N Z-phase

All new 9-12%Cr creep resistant steels developed in the last 35 years contain balanced additions of Nitrogen (0.03-0.07wt%) and nitride formers V (0.2-0.25wt%) and Nb (0.05-0.07 wt%). This development was mainly due to Fujita [8], and it led to excellent

microstructure stability of 9-10%Cr steels, since fine nano-sized (V,Nb)N nitrides are stable against coarsening up to 10^5h at 600-650°C, and contribute significantly to the long-term creep strength.

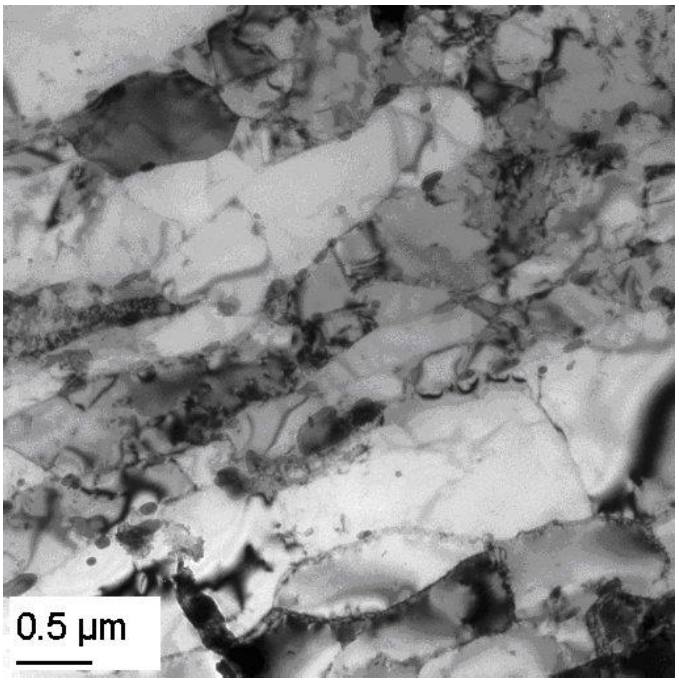

Figure 1. Steel Grade 92.Tempered martensite microstructure as observed in Transmission electron microscope (TEM)

However, it is now well understood that Z-phase nitrides Cr(V,Nb)N are thermodynamically more stable than the (V,Nb)N nitrides, and that a nitride transformation from (V,Nb)N to Z-phase can take place in the 9-12%Cr steels. Since the Cr(V,Nb)N Z-phase nitrides can grow fast to very large (micron) sizes, the Z-phase transformation with elimination of the fine (V,Nb)N nitrides can lead to a significant loss of precipitation strengthening [9-12].

Systematic investigations of a large number of 9-12%Cr steels have revealed kinetics, driving forces and transformation mechanisms for the Z-phase transformation [11-13]. It is clear that increased Cr content strongly accelerates the transformation. In 11-12% Cr steels, the transformation is often complete before 30,000 hours at 600ºC, whereas in 9-10%Cr steel it can take several 100,000 hours. This explains the lack of success to develop stable 11-12%Cr steel, which bases high creep strength on (V,Nb)N nitride precipitates.

3.0 NEW STEEL DEVELOPMENTS

In recent years there has been good progress in the development of new 9-10%Cr steels, which show good prospects to reach improved creep properties as compared to steel P92 and FB2, Table 1 and Fig. 2. However, for applications at steam temperatures above 620°C the 9-10%Cr steels will need surface coatings for oxidation protection.

The TAF steel developed by Fujita in the 1950s based on 10.5wt%Cr and high Boron of 400 ppm is still among the strongest martensitic creep resistant steels [14]. Due to its high Boron content it has limited practical applicability, but it serves as a target line for new steel developments.

	P92	FB2	TAF	BH	MARBN				Belgorod
Mass %					**NIMS**	**NPM1**	**NPM2**	**MARBN12**	
C	0.11	0.13	0.18	0.03	0.078	0.074	0.090	0.081	0.10
Si	0.10	0.05	0.50	0.36	0.31	0.29	0.30	0.30	0.06
Mn	0.45	0.82	1.0	0.49	0.49	0.44	0.51	0.53	0.10
Cr	8.82	9.32	10.5	9.12	8.88	9.26	9.26	9.09	10.0
Mo	0.47	1.47	1.5	0.15	-	-	-	-	0.70
W	1.87	-	-	2.40	2.85	2.84	2.92	2.62	2.0
Ni	0.17	0.16	0.1	0.01	-	0.06	-	<0.01	0.17
Co	-	0.96	-	1.8	3.00	2.95	2.88	3.02	3.0
V	0.19	0.20	0.2	0.20	0.20	0.21	0.20	0.21	0.20
Nb	0.06	0.05	0.15	0.05	0.051	0.056	0.050	0.052	0.05
Ti	-	-	-	-	-	-	-	-	0.01
N	0.047	0.019	0.02	0.050	0.0079	0.013	0.010	0.0072	0.003
B	0.0020	0.0085	0.0400	0.0060	0.0135	0.0120	0.0100	0.0110	0.0080
Norm	1070ºC	1100ºC	1150ºC	1050ºC	1150ºC	1150ºC	1150ºC	1100^{0}C	1060ºC
Temp		570ºC							
	780ºC	710ºC	700^{0}C	780ºC	770^{0}C	770^{0}C	770^{0}C	800^{0}C	770^{0}C

Table 1. Chemical composition (Mass%, bal. Fe) and heat treatment of new 9-10%Cr steels.

3.1 9CrWCoB steels (MARBN)

Currently, much attention is focused on the developments by NIMS of MARBN steels, which are 9Cr3Co3WVNbB steels alloyed with 100-140 ppm of Boron, and with reduced amount of N around 0.010 wt% [15] Creep data up to 40,000 h/650^{0}C have recently been published [16,17], and European researchers have taken up the development of the MARBN steel [18, 19].

The MARBN steels rely mainly on stabilization of $M_{23}C_6$ by Boron and on strengthening by fine (V,Nb)N Nitrides. However, the MARBN steels can also be sensitive to Z-phase formation even though they contain only 9%Cr. After 24,000 hours at 100MPa/650^{0}C, Z-phase formation and dissolution of (V,Nb)N nitrides was found in the NPM1 steel [18, 20]. As seen in Fig. 2 this led to a loss of creep strength, which implies that precipitation hardening by fine MN nitrides contributes significantly to the strengthening of the MARBN steels. However, with adjustments of the composition as in the NPM2 and MARBN12 steels, table 1, it seems possible to delay the Z-phase formation, and the MARBN steel could reach the strength level of TAF, Figure 2

3.2 Low C 9CrWCo steel (BH)

The BH steel contains similar Nitrogen, but a reduced amount of C and increased Boron and Co as compared with steel P92, Table 1. This steel shows better creep performance than the TAF steel at 100MPa/650^{0}C, and excellent microstructure stability up to 50,000 hours at 650^{0}C, Fig. 2 [21]. However, in the long term around 80,000 hours Z-phase transformation is also observed in this steel, and the strength drops to the level of TAF.

3.3 Z-phase in new 9CrWCo steels

In summary, creep strength of the new 9CrWCo steels MARBN and BH rely more or less on precipitation strengthening by fine MN nitrides. This is lost by Z-phase precipitation in the long-term range, whereby the creep strength is reduced. It has been found that contents of Ni and Co in 9-10%Cr steels accelerate the Z-phase transformation significantly [22-24]. The improved long-term performance of the BH steel compared to the MARBN steels could thus be caused by the reduced Co content of 1.8 wt.% as compared to the 3 wt.% in the MARBN steels. This significantly delays the formation of Z-phase in the BH steel.

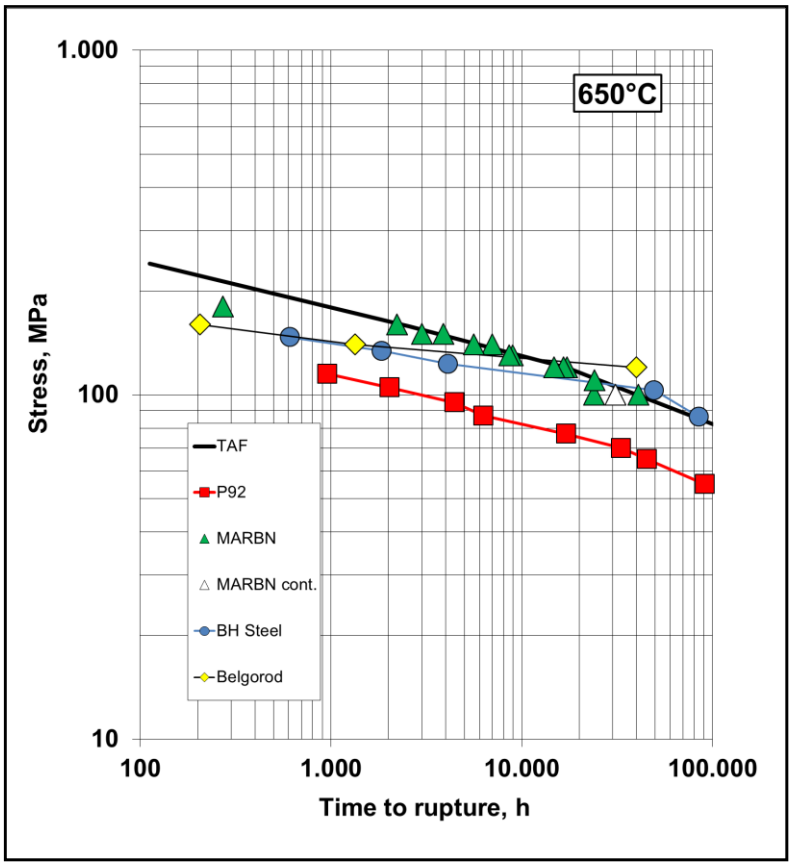

Figure 2. Creep rupture strength of new 9-10%Cr steels.

4.0 Z-PHASE STRENGTHENED 12%Cr STEEL

The Z-phase transformation effectively prevents the development of strong stable 11-12%Cr steels, which rely on precipitation of fine (V,Nb)N nitrides for high creep strength. This means that a development strategy for 11-12%Cr steels has to rely on other precipitates than (V,Nb)N. This could involve either using the Z-phase itself as a strengthening agent or elimination of the Z-phase from the steels.

The formation mechanism for Z-phases is not traditional nucleation and growth like most other precipitate phases. Instead, the Z-phase forms only by diffusion of Cr into pre-existing MN nitrides. Coarse Z-phases form by fast growth of fully transformed particles, including the consumption of other fine MN, which dissolve [25-27]. This understanding led to the idea that a strong acceleration of the Z-phase transformation could provide a fine distribution of Z-phase particles with high particle strengthening. Considerations indicated that Z-phase coarsening would be rather similar to MN [28].

Driving force calculations by thermodynamic modelling indicated that steels with low carbon content and high Cr content could show fast transformation of Nb or Ta based MN into Z-phase [13], and test alloys were designed, Table 2.

	wt%, bal. Fe											
	Cr	C	B	Ta	Nb	N	W	Ni	Co	Cu	Mn	Si
Z3	11,64	0,005	0,004	0	0,26	0,036	2,82	1,47	5,4	0	0,49	0,3
Z4	11,79	0,005	0,004	0,39	0	0,033	2,9	0,5	7,3	0	0,48	0,3
ZL3	12,1	0,06	0,0063	0,36	0	0,049	2,47	0,19	3,5	1,95	0,21	0,31

Table 2. Chemical compositions of the first Z-phase strengthened steels.

Experiences with the first test alloys of Z-phase strengthened steels revealed basic challenges:

- The steel should have high Cr and very low carbon content in order to form only nitrides, which can transform fast into Z-phase
- High Cr content and low carbon content will stabilize δ-ferrite.
- Elements, which suppress δ-ferrite (stabilize austenite), lower the Ac1 temperature.
- Low carbon removes Cr carbides from the steel. Thus, other precipitates should be added for strength.

Isothermal annealing experiments showed that CrTaN Z-phases were stable against coarsening up to 10,000 hours at 650ºC, Fig. 3. CrNbN Z-phases in steel Z3 were found to be less stable. The increase of Carbon content in steel ZL3 led to slower Z-phase transformation and coarser CrTaN Z-phase particles. The higher Carbon means that Ta(C,N) forms instead of TaN, and this has to get rid of Carbon in the transformation to CrTaN.

The low carbon content in Z-phase forming steels means that no or only very small amounts of $M_{23}C_6$ carbides form in the steels. Instead, high amount of W is added in order to form Laves phase $(Fe,Cr)_2W$ for precipitation hardening. However, in the Z4 steel the Laves phase precipitated in a continuous film along prior austenite grain boundaries during tempering. Consequently, this steel had very low impact toughness at room temperature. The ZL3 steel has lower W content and good impact toughness.

Creep tests on steel Z4 show strength similar to steel P92 up to more than 10,000 hours, Fig. 3. The ZL3 steel with improved toughness show lower strength between P91 and P92 due to slow Z-phase transformation and lower content of Laves phase. Ongoing research aims to optimize Carbon, Co and W contents in the steels. Results so far indicate that higher creep strength than for steel P92 can be achieved [29].

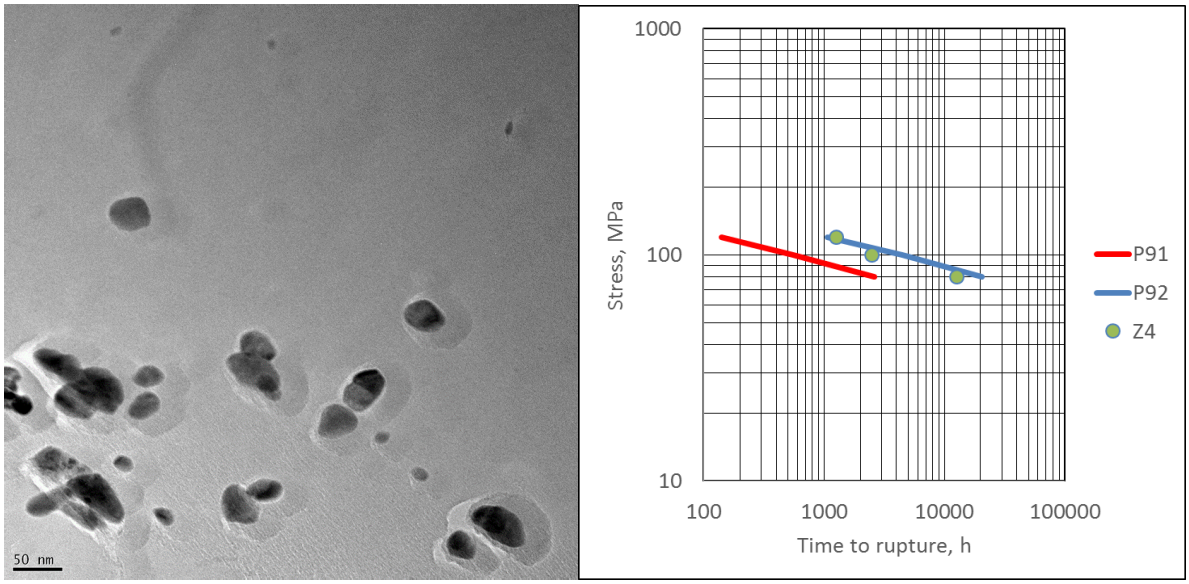

Figure 3. Fine CrTaN Z-phase particles in steel Z4 after ageing 650ºC/10,000h (left) and creep rupture tests on steel Z4 at 650ºC (right)

5.0 Z-PHASE FREE 12%Cr STEEL

Another option to design a strong stable 12%Cr steel is to eliminate nitrides, which could transform into Z-phase. It is known that only V, Nb and Ta based MN nitrides can transform to Z-phase CrMN [30].

Belgorod state university designed a 10%Cr steel, which shows excellent creep stability up to more than 35,000 hours at 650^0C/120MPa, Table 1 and Fig. 2. The results indicate that this steel could reach the creep strength target of 100 MPa for 10^5h at 650°C [31-33]. Alloy design is based on the TOS 110 steel earlier developed at Toshiba [34], but the composition has been altered with reduced Nitrogen and addition of Titanium. This means that TiN is the only nitride, which forms in the steel, and TiN cannot transform into Z-phase. Thus, the elimination of the Z-phase transformation could be an explanation for the excellent long-term microstructure stability of the Belgorod steel. The exact strengthening mechanism of the steel without (V,Nb)N nitrides is still under investigation. The TiN nitrides are not expected to contribute significantly to the strength.

The elimination of Z-phase transformation means that it could be possible to increase the Cr content of such steels without introducing microstructure instability. Work is ongoing to design and test a 12%Cr steel based on the ideas to eliminate nitrides, which could transform into Z-phase.

6.0 SUMMARY

There is a need to develop strong stable creep resistant steels in order to increase steam temperatures of coal-fired power plants up to 650°C. 12% of Cr is needed for protection against steam oxidation at this temperature. However, all previous 12%Cr steels containing fine (V,Nb)N for precipitation strength suffered breakdowns in long-term creep due to formation of coarse Cr(V,Nb)N Z-phase. Future stable 12%Cr steels need to be based on other strengthening phases than (V,Nb)N nitrides.

Coarse Z-phases may form during long-term creep in 9%Cr steels with Co contents of 1.8% and higher.

Attempts were made to use fine CrNbN or CrTaN Z-phases for strengthening. It has been shown that such particles can be controlled to form on a fine scale in 12%Cr steels with low Carbon content.

Alloy design of low Carbon 12%Cr steels offer challenges to control δ-ferrite, Laves phase and toughness in order to obtain high strength and microstructure stability.

Another option for strong stable 12%Cr steels is to eliminate MN nitrides based on V, N or Ta, so Z-phase cannot form. Alloying with Ti in order to tie up the nitrogen in low N steels is a promising concept, which is now explored.

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